Applied Geochemistry 40 (2014) 135–143

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

The interactions of strontium and technetium with Fe(II) bearing biominerals: Implications for bioremediation of radioactively contaminated land

Clare L. Thorpe [a], Christopher Boothman [a], Jonathan R. Lloyd [a], Gareth T.W. Law [a,b], Nicholas D. Bryan [a,b], Nick Atherton [c], Francis R. Livens [a,b], Katherine Morris [a,*]

[a] Research Centre for Radwaste and Decommissioning and Williamson Research Centre for Molecular Environmental Science, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Manchester M13 9PL, UK
[b] Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Manchester M13 9PL, UK
[c] Sellafield Ltd., Land Quality, Sellafield, Seascale, Cumbria CA20 1PG, UK

ARTICLE INFO

Article history:
Received 19 July 2013
Accepted 12 November 2013
Available online 20 November 2013
Editorial handling by D. Fortin

ABSTRACT

At nuclear contaminated sites, microbially-mediated Fe(III) reduction under alkaline conditions opens up the potential for co-treatment of the groundwater contaminants ^{99}Tc, though reduction to less mobile Tc(IV) phases, and ^{90}Sr, through increased sorption and/or precipitation promoted at higher pH. In the experiments described here, microbial enrichment cultures derived from representative Sellafield sediments were used to probe the effect of microbially-mediated Fe(III) reduction on the mobility of ^{99}Tc and Sr (as stable Sr^{2+} at elevated concentrations and $^{90}Sr^{2+}$ at ultra-trace concentrations) under both neutral and alkaline conditions. The reduction of Fe(III) in enrichment culture experiments at an initial pH of 7 or 9 resulted in the precipitation of an Fe(II) bearing biomineral comprised of siderite and vivianite. Results showed that TcO_4^- added at 1.6×10^{-6} M was removed (>80%) from solution concurrent with Fe(III) reduction at both pH 7 and pH 9. Furthermore, X-ray absorption spectroscopy of the reduced biominerals confirmed reduction of Tc(VII) to Tc(IV). To understand Sr behaviour in these systems, Sr^{2+} was added to enrichment cultures at ultra-trace concentrations (2.2×10^{-10} M (as $^{90}Sr^{2+}$)) and at higher concentrations (1.15×10^{-3} M (as stable Sr^{2+})). In ultra-trace experiments at pH 7, microbially active systems showed enhanced removal of ^{90}Sr compared to the sterile control. This was likely due to sorption of $^{90}Sr^{2+}$ to the Fe(II)-bearing biominerals that formed *in situ*. By contrast, at pH 9, the sterile control showed comparable removal of ^{90}Sr to the microbially active experiment even though the Fe-minerals formed were of very different character in the active (vivianite, siderite) versus sterile (an amorphous Fe(III)-phase) systems. Overall, ^{90}Sr bioreduction experiments showed 60–70% removal of the added ^{90}Sr across the different systems: this suggests that treatment strategies involving bioreduction and the promotion of Fe(III)-reducing conditions to scavenge Tc(IV) are not incompatible with treatment of groundwater ^{90}Sr contamination. In systems with elevated Sr^{2+} concentrations and an initial pH of 7, microbially active systems showed <20% removal of added Sr^{2+} following Fe(III) reduction with little or no removal in sterile controls. At pH 9, significant Sr^{2+} was removed from solution in both sterile and microbially active experiments and was attributed to Sr-sorption to mineral phases both chemically precipitated in sterile controls, and biologically precipitated in the microbially active systems. These results confirm that in systems with an elevated natural or anthropogenic Sr^{2+} loading, bioreduction at modestly alkaline pH is compatible with co-treatment of both TcO_4^- and $^{90}Sr^{2+}$. These data are discussed in terms of aqueous geochemistry trends, X-ray diffraction and morphological data, and thermodynamic modelling. The results demonstrate the potential for removal of trace levels of ^{99}Tc and $^{90}Sr^{2+}$ from groundwaters during stimulated bioreduction and highlight that in the presence of stable Sr^{2+}, optimal removal for technetium and strontium is likely to occur under mildly alkaline, reducing conditions.

1. Introduction

Management of the global radioactive waste legacy is a subject of intense public and political concern and many nuclear sites have significant subsurface radioactive contamination. Safe management of these complex contaminated sites, which represent major

* Corresponding author. Tel.: +44 (0)161 275 7541.
E-mail address: katherine.morris@manchester.ac.uk (K. Morris).

0883-2927
http://dx.doi.org/10.1016/j.apgeochem.2013.11.005

financial liabilities, is essential as they pose significant risks to society. Strontium-90 and technetium-99 are abundant radionuclides in radioactive wastes and are also common co-contaminants in the subsurface at nuclear facilities including at the Sellafield (UK), Oak Ridge- and Hanford-(USA) sites (McBeth et al., 2007; McKenzie et al., 2011; Poston et al., 2011). With a half-life of 29 years, ^{90}Sr is of concern from a contaminated land perspective and is present at elevated concentrations in groundwaters at Sellafield (McKenzie et al., 2011; Thorpe et al., 2012a; Wallace et al., 2012). In contrast, ^{99}Tc (half-life 2.14×10^5 years) which is also present in groundwaters at Sellafield (McKenzie et al., 2011), will be relevant over an extended time, making its behaviour pertinent to both contaminated land and radioactive waste geological disposal scenarios. Furthermore, both radionuclides are problematic because of their relatively high environmental mobility and their differing biogeochemical behaviour which makes co-treatment *via* traditional techniques challenging. Technetium-99 is a redox active radionuclide and its mobility can be attenuated by reduction from soluble Tc(VII) to poorly soluble Tc(IV) (Lloyd et al., 2000; Burke et al., 2005). In contrast, the mobility of the $^{90}Sr^{2+}$ ion is primarily controlled by sorption and mineral precipitation reactions (Langley et al., 2009; Thorpe et al., 2012a; Wallace et al., 2012, 2013).

Biostimulation of Fe(III)-reducing conditions in the subsurface has been identified as a potential mechanism for immobilising aqueous ^{99}Tc under circumneutral conditions (Istok et al., 2004; Law et al., 2010). Here, Tc(VII) reduction to Tc(IV) proceeds indirectly *via* an abiotic reaction with Fe(II)-bearing minerals (Lloyd et al., 2000; Burke et al., 2005; Plymale et al., 2011). Indeed, several studies have shown that Tc(VII) is reduced and largely immobilised as hydrous TcO_2 like phases on contact with a range of Fe(II)-bearing minerals (e.g. Lloyd et al., 2000; Morris et al., 2008; Peretyazhko et al., 2008; McBeth et al., 2011). Furthermore, in recent experiments using ^{99m}Tc as a tracer at environmentally relevant concentrations ($\sim 10^{12}$ M; below the solubility limit for hydrous TcO_2 at circumneutral pH), Tc(VII) was retained on Fe(III)-reducing sediments presumably *via* reductive sorption of Tc(IV) (Lear et al., 2010; Burke et al., 2010; Vandehey et al., 2012). In contrast, relatively few studies have considered the effect of Fe(III) reduction and the subsequent changes in mineralogy and geochemistry on the mobility of $^{90}Sr^{2+}$, despite the fact this radionuclide is often a co-contaminant with technetium. Indeed, whist bioreduction is a clear treatment pathway for technetium its implications for $^{90}Sr^{2+}$ treatment are poorly constrained.

Under oxic conditions, poorly crystalline Fe(III) oxyhydroxides are known to be an important sink for metal cations including Sr^{2+}, and some studies have reported that Fe(III) reduction can result in release of Sr^{2+} to solution (Ferris et al., 2000; Langley et al., 2009). By contrast, other workers report removal of Sr^{2+} from solution concurrent with Fe(III) reduction (Ferris and Roden, 2000; Parmar et al., 2000; Roden et al., 2002). Clearly understanding the behaviour of Sr during bioreduction will inform the potential for bioremediation deployment on $^{90}Sr^{2+}$ and ^{99}Tc contaminated nuclear sites. In a recent sediment microcosm bioreduction study, extensive denitrification led to a raised pH (>9) and Fe(III) reduction developed under alkaline conditions (Thorpe et al., 2012a). In that experiment, elevated Sr^{2+} (>1.15 mM) was removed from solution as bioreduction proceeded through to Fe(III) reduction in sediments, with strontium removal in these dynamic systems attributed both to increased Sr^{2+} sorption due to a rise in pH, and to Sr^{2+} incorporation in newly formed carbonate phases (Thorpe et al., 2012a). Thus, denitrification has been shown to prime sediments for Fe(III) reduction under mildly alkaline conditions: this opens up the suggestion that co-treatment of ^{99}Tc and $^{90}Sr^{2+}$ by stimulated bioreduction at mildly alkaline pH may be possible. Indeed, recent work shows that microbial communities can adapt to develop a cascade of terminal electron accepting processes at higher environmental pH conditions favourable to both ^{99}Tc and $^{90}Sr^{2+}$ treatment (Stewart et al., 2010; Whittleston et al., 2011; Rizoulis et al., 2012; Williamson et al., 2013). Nonetheless, to our knowledge few studies have examined the behaviour of Sr^{2+} and ^{99}Tc under bioreduction conditions at elevated pH. This is despite the fact that these conditions are pertinent to co-treatment scenarios for bioremediation of radioactively contaminated land and, for ^{99}Tc, to geological disposal. Reflecting this, we have used a microbial culture enriched from Fe(III)-reducing sediments representative of the Sellafield nuclear facility to reductively precipitate an Fe(II)-bearing biomineral assemblage at both neutral and alkaline pH. This enrichment culture approach was then used to assess the behaviour of $^{99}TcO_4^-$, $^{90}Sr^{2+}$ and Sr^{2+} during microbial Fe(III) reduction and resultant geochemical change and Fe(II) mineral precipitation in these model systems.

2. Materials and methods

2.1. Isolation of Fe(III)-reducing enrichment culture

An enrichment culture of Fe(III)-reducing microbes able to grow under alkaline pH conditions (pH 9) was obtained from sediment microcosms representative of the Sellafield site. A sediment slurry containing indigenous microbes was transferred (anaerobically, 10% v/v) to serum bottles containing a standard fresh water growth medium (Lovley et al., 1991) that had been adjusted to pH 9 *via* 1 M NaOH addition (Thorpe et al., 2012b). The growth medium contained 30 mM soluble Fe(III)-citrate as the sole electron acceptor, and yeast extract (2 g L^{-1}) as the electron donor and also contained 4 mM phosphate. Sub-aliquots (10% v/v) of the enrichment culture were then transferred to fresh medium every 6 weeks. After six consecutive subcultures, 16S rRNA gene analysis (method as described in Thorpe et al. (2012b)) was performed on the microbial community. This characterised, stable enrichment culture was then maintained in the pH 9 medium by transfer to fresh medium every 6 weeks. A sub-aliquot of the stable pH 9 enrichment was then used to establish a separate Fe(III)-citrate enrichment culture at pH 7. The pH 7 system used the same freshwater medium containing Fe(III)-citrate (30 mM) and yeast extract (2 g L^{-1}), and the pH was adjusted to pH 7 prior to inoculation. Both enrichment cultures were then used to establish a range of ^{99}Tc, stable Sr^{2+}, and $^{90}Sr^{2+}$ experimental systems.

2.2. Mineralogy in enrichment cultures

X-ray diffraction was used to identify the mineral products that formed in the enrichment cultures (Bruker D8Advance). Environmental Scanning Electron Microscopy with Secondary Electron Detection (SED) was used to image the morphology of any mineral products (Phillips XL30 ESEM-FEG) and Energy Dispersive X-ray Spectroscopy (EDX) was used to assess the elemental composition.

2.3. Addition of TcO_4^-, $^{90}Sr^{2+}$ and Sr^{2+} to enrichment cultures

Three different experimental systems were established. Here, ^{99}Tc, $^{90}Sr^{2+}$ or stable Sr^{2+} were added to the pH 7 and pH 9 enrichment cultures at points: (i) with the addition of the enrichment culture to oxic, soluble Fe(III)-citrate medium (progressive enrichment systems); or (ii) after 45 days incubation when the enrichment culture had already formed Fe(II)-bearing biominerals (endpoint enrichment systems). In the progressive enrichment systems, time-course samples were taken over extended periods (45 days). For the end point enrichment systems, ^{99}Tc, $^{90}Sr^{2+}$ or stable Sr^{2+} were added after 45 days of incubation and thereafter,

the geochemistry was tracked for the following 45 days. Technetium, $^{90}Sr^{2+}$ and stable Sr^{2+} additions were performed as follows: ^{99}Tc as NH_4TcO_4 at 1.6×10^{-6} M (100 Bq ml^{-1}); strontium as $^{90}SrCl_2$ at 2.2×10^{-10} M (100 Bq ml^{-1}) or as stable $SrCl_2$ at 1.2×10^{-3} M. The experiments were prepared in 30 ml glass serum bottles with an argon headspace and with the initial pH set to either 7 or 9 prior to inoculation with the enrichment culture. All experimental systems were prepared in triplicate. Sterile controls were also run without triplicate analysis. After inoculation, experiments and sterile controls were monitored for pH, $Fe_{(aq)}$, 0.5 N HCl extractable solid Fe(II)/Fe(III), and ^{99}Tc, $^{90}Sr^{2+}$ or Sr^{2+} as required.

2.4. Sampling and geochemical analysis

Geochemical analyses were performed on subsamples withdrawn anaerobically using aseptic technique. The ratio of Fe(II) to Fe(III) in samples was determined by dissolution of 0.1 ml unfiltered biomineral slurry for 1 h in 0.5 N HCl followed by ferrozine analysis (Lovley and Phillips, 1986). Anions, HCO_3^- and CO_3^{2-}, were measured by ion chromatography and pH was measured with a pH meter and calibrated electrode. Aqueous ^{99}Tc and $^{90}Sr^{2+}$ were quantified using liquid scintillation analysis. Here, a 0.5 ml aliquot of centrifuged (10 min, 2600*g*) sample was analysed on a Packard Tri-Carb 2100TR so that the counting error was less than 2%. The detection limit of the instrument (~0.4 Bq per sample under typical counting conditions) was <1% of the total activity added for both ^{99}Tc and ^{90}Sr (100 Bq ml^{-1}). Aqueous, stable Sr was measured by ICP-OES (Perkin Elmer Optica 5300) using matrix matched standards. Here, the detection limit of $\sim 1 \times 10^{-6}$–1×10^{-7} M was <0.001% of the initial Sr added.

2.5. Thermodynamic modelling

Speciation modelling was performed in PHREEQC-2 using the Lawrence Livermore National Laboratory database. The initial solution chemistry used was based around the modified freshwater medium: Fe (2.85×10^{-2} M), C (1.73×10^{-1} M), Na (3.38×10^{-2} M), Cl (6.28×10^{-3} M), P (3.92×10^{-3} M), K (1.35×10^{-3} M), Mg (2.9×10^{-4} M), S (2.5×10^{-4} M), and Mn (2.9×10^{-5} M). The temperature for modelling was set at 21 °C and the pH was as measured. The background stable Sr^{2+} present in the system (e.g. from reagents and the yeast extract) was estimated to be at sub-μM concentrations.

2.6. Sequential extractions

In order to further explore the fate of Sr^{2+} and $^{90}Sr^{2+}$ in the experiments, sequential extraction experiments were performed on Sr^{2+} amended progressive-, $^{90}Sr^{2+}$ amended progressive-, and $^{90}Sr^{2+}$ amended end point-enrichment systems. For each experimental system, the aqueous phase was separated from the solid phase by centrifugation (10 min, ~2600*g*) and the Sr^{2+} or $^{90}Sr^{2+}$ concentration was measured in the aqueous phase. Sequential extractions were performed in triplicate on the remaining moist pastes from the whole experiment using an extraction series based on Tessier et al. (1979) and Keith-Roach et al. (2003), under an anaerobic atmosphere and using 50 ml of leaching solution in each step. Steps comprised: (i) 1 M magnesium chloride at pH 7 agitated for 2 h: the "exchangeable" fraction; (ii) 1 M sodium acetate at pH 4.5 agitated for 24 h: "carbonate associated" phases; and (iii) 0.2 M ammonium oxalate at pH 4.8 agitated for 2 h: "reducible" phases. By the end of 0.2 M ammonium oxalate extraction, no residual biomineral was visible and no further extraction steps were performed. Sequential extraction data are presented as a percentage of total Sr^{2+}/$^{90}Sr^{2+}$ and Fe in the different systems at 45 days: aqueous, exchangeable, extractable and reducible.

2.7. X-ray absorption spectroscopy

X-ray Absorption Spectroscopy (XAS) was used to determine directly the average speciation of ^{99}Tc in the biomineral samples from end point enrichment systems at pH 7 and 9. Here, 250 kBq of $^{99}TcO_4^-$ was added to 10 ml serum bottles containing ~0.5 g of reduced biomineral produced in the enrichment cultures and samples were equilibrated for 14 days to allow reaction. Moist biomineral pastes were then packed into triple contained sample holders under anaerobic conditions and stored at −80 °C in sealed jars under an Ar atmosphere until analysis. An NH_4TcO_4 solution provided a Tc(VII) standard for comparison. Technetium K-edge XANES and EXAFS data were collected on the B18 beamline at the UK DIAMOND synchrotron at ambient temperature and in fluorescence mode, using a nine-element Ge solid-state detector. Multiple Q-EXAFS scans (>30) were then averaged in Athena (Ravel and Newville, 2005), background subtracted in PySpline (Tenderholt et al., 2007), and fitted using DL_EXCURV (Tomic et al., 2005) using full curved wave theory (Gurman et al., 1984). Here, using the relevant literature, shells of backscatterers were added around the Tc absorber atom and a best fit was achieved by refining the Fermi energy, the absorber–scatterer distance, and the Debye–Waller factor for each shell. Shells were only included if their addition caused the least square residual (the *R*-factor) to be improved by >5% (Binsted et al., 1992).

3. Results and discussion

3.1. Fe(III) reduction in enrichment cultures

The stable microbial community used to establish all of the $^{99}TcO_4^-$, Sr^{2+} and $^{90}Sr^{2+}$ amended pH 7 and pH 9 enrichment cultures comprised >98% abundance of close relatives of the class *Clostridia* (with >95% 16S rRNA sequence homology; Supporting Information Table A). Members of the *Clostridiales* are known to reduce Fe(III) in freshwater and marine environments over a wide pH range either *via* dissimilatory Fe(III) reduction (e.g. Dobbin et al., 1999) or by using Fe(III) as a minor electron acceptor during fermentation (Lovley and Phillips, 1988; Stewart et al., 2010; Lehours et al., 2010).

In sterile controls at pH 7, an Fe(III)-citrate aqueous complex persisted over the course of the experiment and there was no evidence for precipitation of Fe(III)-minerals. In the enrichment cultures with an initial pH of 7, the pH remained steady throughout the experiments. In these systems Fe(III) citrate was initially soluble, but once inoculated, an ephemeral Fe-bearing precipitate was observed during the first week of incubation suggesting possible breakdown of the Fe(III)-citrate complex (Francis and Dodge, 1993). After further incubation (25 days), 0.5 N HCl extraction of the mineral slurry showed that >95% of extractable Fe(III) had been reduced to Fe(II). After 45 days, ~40% of the total Fe remained in solution as Fe(II) and a biomineral precipitate was evident. Analysis by XRD of the biomineral confirmed the presence of Fe(II)-bearing siderite ($FeCO_3$) and vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) (Fig. A, Supporting Information). The medium contained elevated (4 mM) phosphate, and we note that phosphate is also present at elevated concentrations at the Sellafield site (McKenzie et al., 2011) and that vivianite is also significant within some high productivity environmental settings (Konhauser, 1997; Islam et al., 2005). The morphology and elemental composition of the solids showed aggregates of both Fe-rich cubic crystals that are typical of siderite morphology and large prismatic, often radiating, iron/phosphate rich crystals that are typical of vivianite (Fig. B, Supporting Information). Geochemical analyses coupled to sequential extractions on these experiments showed that of the total Fe in the

system at the experiment end point, ~40% of the Fe was present in solution as $Fe(II)_{(aq)}$, ~5% of Fe was in the exchangeable fraction, 40–50% was in the carbonate associated fraction, and the remaining ~10% was in the reducible fraction.

In sterile controls at pH 9, an amorphous abiotically formed Fe(III)-bearing precipitate was present by 24 h and persisted over 45+ days. In enrichment cultures with an initial pH of 9, the pH decreased to pH 8.5–8.7 during the incubation presumably due to an increase in acidity due to CO_2 release during microbial respiration, and/or the consumption of OH^- and HCO_3^- during $FeCO_3$ precipitation. After inoculation and subsequent incubation for 45 days, XRD showed that the pH 9 systems had precipitated a siderite/vivianite-containing biomineral phase (Fig. A, Supporting Information). Again, the morphology and elemental composition of these end point samples was confirmed using SEM and EDAX (Fig. B, Supporting Information). Sequential extractions suggested that in this experiment by 45 days, <1% of the total iron in the system remained soluble, <1% of Fe was in the exchangeable fraction, ~80% was in the carbonate associated fraction, and ~20% was in the reducible fraction.

3.2. Technetium-99 behaviour during Fe(III) reduction

3.2.1. Technetium-99 behaviour at pH 7

In the pH 7 oxic sterile control amended with 1.6×10^{-6} M $^{99}TcO_4^-$, both Fe (as Fe(III)-citrate) and ^{99}Tc remained in solution over 45 days (Fig. 1A). In the pH 7 progressive enrichment systems, ^{99}Tc was removed from solution during Fe(III) reduction with 86.9 ± 11.7% of ^{99}Tc associated with the solid phase by 45 days (Fig. 1A). In end point enrichment systems, where TcO_4^- was exposed to the pre-reduced biomineral, 83.0 ± 2.2% of the added ^{99}Tc was removed by 45 days (Fig. 1C). In pH 7 end point experiments amended with elevated levels of ^{99}Tc for XAS analysis, removal of TcO_4^- was consistent with low level experiments and the XANES spectra (data not shown) of the biomineral clearly matched Tc(IV) spectra reported in other studies (e.g. Wharton et al., 2000; Morris et al., 2008). This confirmed reductive precipitation to Tc(IV). Background subtracted, k^3 weighted EXAFS spectra and Fourier transforms (Fig. 2 and Table 1) were best fit with a first shell of 6 O atoms at 2.0 Å (characteristic of TcO_2; Wharton et al., 2000), and a second shell of 1 Tc atom at 2.46 Å. This provided a marginally better second shell fit than 1 Fe atom at 2.63 Å and reflecting this, the data are comparable with the hydrous TcO_2 like phases as described by Morris et al. (2008) (Table 1). The addition of a third shell of 6 O atoms at 3.95 Å also significantly improved the fit and was consistent with the model for polymeric TcO_2 presented by Lukens et al. (2002) (Table 1). Interestingly, in both progressive enrichment systems and endpoint enrichment systems ~15% of ^{99}Tc remained in solution after 45 days incubation despite a vast excess of Fe(II) in the system and similar to recent observations on Fe(II) biomineral systems at circumneutral pH (McBeth et al., 2011). It is possible that TcO_4^- may be recalcitrant to reductive precipitation and/or Tc(IV) may be relatively soluble in these systems as recent work has highlighted the potential for formation of soluble Tc(IV)-carbonate complexes or Tc(IV)-citrate complexes (Alliot et al., 2009; Wall and Karunathilake, 2012) and both of these ligands are relevant here.

3.2.2. Technetium-99 behaviour at pH 9

In the pH 9 oxic sterile controls, ^{99}Tc remained in solution throughout 45 days incubation (Fig. 1B). In the pH 9 progressive enrichment culture system, ^{99}Tc removal occurred with 84.7 ± 9.8% of the added ^{99}Tc removed from solution after 45 days of anaerobic incubation (Fig. 1B). In the end point enrichment

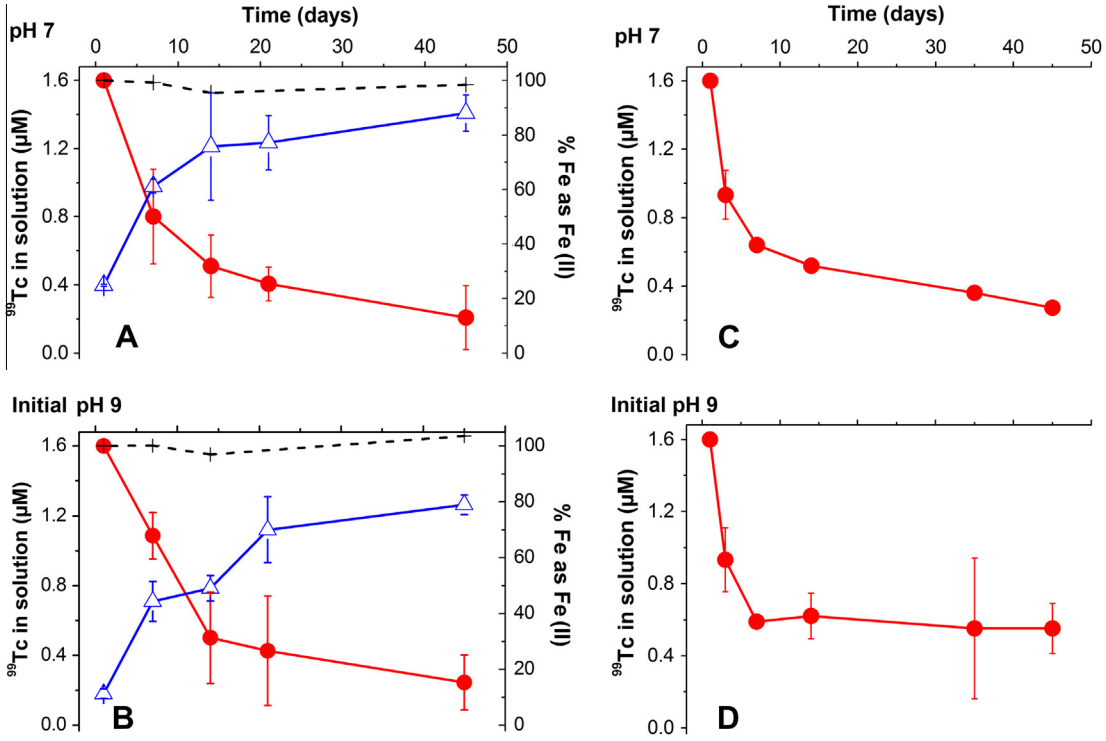

Fig. 1. ^{99}Tc in solution (primary axis) and percentage of 0.5 N HCl extractable Fe present as Fe(II) (secondary axis) for (A) ^{99}Tc amended progressive enrichment systems at pH 7.0; (B) ^{99}Tc amended progressive enrichment systems at an initial pH 9.0; (C) ^{99}Tc amended end point enrichment systems at pH 7.0; and (D) ^{99}Tc amended end point enrichment systems at initial pH 9. Key: ● = ^{99}Tc in solution in inoculated enrichment cultures or biomineral systems, + = ^{99}Tc in solution in corresponding sterile control systems, and △ = % Fe as Fe(II) in progressive enrichment systems. Error bars represent 1σ experimental uncertainty from triplicate analyses (where not visible error bars are within symbol size).

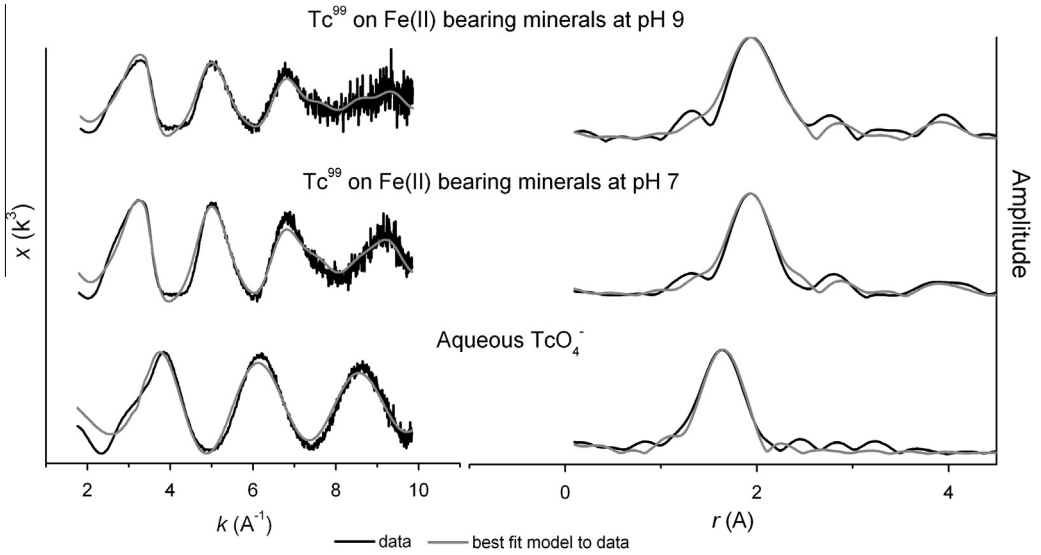

Fig. 2. Experimental (black) and theoretical best fit (light grey) EXAFS spectra and corresponding Fourier transforms obtained for (from top to bottom): (1) ^{99}Tc in end point (45 days) Fe(II) bearing biomineral system at initial pH 9, (2) ^{99}Tc in end point (45 days) Fe(II) bearing biomineral system at pH 7, and (3) TcO_4^-.

Table 1
EXAFS modelling of Tc K-edge spectra for ^{99}Tc associated with Fe(II) bearing biomineral phases at pH 7 and 9 and as pertechnetate.

Sample	Shell	*N*, type	*r* (Å)	$2\sigma^2$ (Å^2)	*R*
TcO_4^-	1	4, O	1.71	0.007	23.7
Fe(II) biomineral system pH 7	1	6, O	2.01	0.019	35.8
	1	6, O	2.00	0.019	30.7
	2	1, Fe	2.63	0.015	
	1	6, O	2.01	0.017	29.7
	2	1, Tc	2.45	0.016	
	1	6, O	2.01	0.018	27.3
	2	1, Tc	2.46	0.021	
	3	6, O	3.95	0.019	
Fe(II) biomineral system initial pH 9	1	6, O	2.01	0.025	52.1
	1	6, O	2.01	0.024	46.5
	2	1, Fe	2.61	0.016	
	1	6, O	2.01	0.022	46.1
	2	1, Tc	2.42	0.018	
	1	6, O	2.01	0.022	43.3
	2	1, Tc	2.44	0.024	
	3	6, O	3.93	0.016	

N is the occupancy, *r* is the interatomic distance, $2\sigma^2$ is the Debye–Waller factor (Å^2) and *R* (least square residual) is a measure of the overall goodness of fit.

systems when TcO_4^- was exposed to the pre-reduced biomineral at pH 9, ^{99}Tc was removed to a somewhat lesser extent: 65.5 ± 8.1% removal after 45 days reaction with the Fe(II)-bearing biominerals (Fig. 1D). The XANES spectra for pH 9 enrichment cultures amended with elevated levels of ^{99}Tc (data not shown) were again typical of Tc(IV) spectra and the EXAFS spectra for the ^{99}Tc exposed to the bio-precipitate at pH 9 were very similar to the pH 7 system suggesting a similar fate for the ^{99}Tc in these two systems (Fig. 2). The data were best modelled by 6 O atoms at ~2.00 Å and with a backscatter of 1 × Tc at 2.45 Å providing a marginally improved fit compared to 1 × Fe at 2.61 Å, again suggesting a partially ordered TcO_2 like phase. Furthermore, as observed in the pH 7 system, the addition of a third shell of 6 O atoms at 3.97 Å did improve the fit significantly (Fig. 2) and was consistent with published fits for short chain TcO_2 like phases (Lukens et al., 2002). Overall these data provide a novel addition to the literature on solid phase Tc-speciation by reporting microbially-mediated Tc(IV) reduction in model Fe(II)-bearing biomineral phases at elevated pH. Furthermore they suggest that bioreduction will provide a useful strategy to significantly reduce ^{99}Tc concentrations in groundwaters across a range of *in situ* pH conditions. Interestingly in these experiments, a modest fraction (~20%) of ^{99}Tc was recalcitrant to removal, again possibly due to poor reduction of TcO_4^- and/or formation of soluble Tc(IV)-carbonates and or Tc(IV)-citrates and this warrants further investigation.

3.2.3. Strontium-90 behaviour during Fe(III) reduction and Fe(II) mineral formation

3.2.3.1. Strontium-90 behaviour at pH 7. In the pH 7 oxic sterile control system amended with 2.2×10^{-10} M (100 Bq ml^{-1}) of $^{90}Sr^{2+}$, the $^{90}Sr^{2+}$ remained in solution (Fig. 3A). In progressive enrichment systems 62.0 ± 6.7%, $^{90}Sr^{2+}$ was removed from solution after 45 days incubation (Fig. 3A). End point enrichment systems, where $^{90}Sr^{2+}$ was exposed to pre-reduced biomineral, removed 45.9 ± 9.5% of the radionuclide following 45 days reaction (Fig. 3C). In these "ultra-trace" $^{90}Sr^{2+}$ systems, PHREEQC-2 predicted under saturation (typically SI = −6; Table 2) with respect to $SrCO_3$ and any removal of $^{90}Sr^{2+}$ is thus likely to be the result of sorption to newly formed Fe(II)-bearing biomineral phases. Furthermore, geochemical analyses coupled to sequential extractions

performed on materials taken from the end point enrichment system indicated that at the end point of the experiment, of the total ^{90}Sr in the system, 37.9 ± 6.7% was in solution, 11.5 ± 4.3% was in the exchangeable fraction, 6.2 ± 1.1% was in the carbonate associated fraction, and 46.1 ± 5.0% was in the reducible fraction. Thus, over 50% of $^{90}Sr^{2+}$ was relatively strongly associated with the newly formed biomineral assemblage.

3.2.3.2. Strontium-90 behaviour at pH 9. In the pH 9 oxic sterile control system, 55.2% of the ^{90}Sr was removed over 45 days incubation (Fig. 3B). Geochemical analysis confirmed that no Fe(III) reduction had taken place, and therefore $^{90}Sr^{2+}$ removal was attributed to its sorption to the X-ray amorphous Fe(III)-bearing precipitate present that formed at pH 9. In the progressive enrichment systems at pH 9, 67.2 ± 2.4% of the added $^{90}Sr^{2+}$ (marginally more than in the sterile control) was removed from solution after 45 days of incubation and in the presence of Fe(II)-bearing minerals (Fig. 3B). In end point experiments, where the $^{90}Sr^{2+}$ was exposed to pre-formed Fe(II)-bearing biominerals, $^{90}Sr^{2+}$ removal was 61.1 ± 5.6% (Fig. 3D). These results suggest that sorption at pH 9 was significant as the system was predicted to be undersaturated with respect to $SrCO_3$ (SI = −4.46; Table 2). Geochemical analyses coupled to sequential extractions performed on materials taken from the end point enrichment system indicated that of the total $^{90}Sr^{2+}$ in the system, 32.7 ± 5.6% was in solution, 4.4 ± 0.7% was in the exchangeable fraction, 19.2 ± 3.0% was in the carbonate associated fraction, and 44.4 ± 5.0% was in the reducible fraction. As observed in pH 7 systems, >60% of $^{90}Sr^{2+}$ was associated with the carbonate or reducible phases suggesting a strong association with the newly formed Fe(II) biominerals.

3.2.4. Stable strontium behaviour during Fe(III) reduction and Fe(II) mineral formation

3.2.4.1. Stable strontium behaviour at pH 7. In the pH 7 oxic sterile control, where Sr^{2+} at 1.15×10^{-3} M was added to soluble Fe(III)-citrate, within the limits of detection, Sr^{2+} remained in solution throughout the experiment. In the pH 7 progressive enrichment systems, 18.2 ± 2.0% of the added Sr^{2+} was removed to solids after 45 days (Fig. 4A). The Sr^{2+} was transiently removed between 1 and 28 days coinciding with the formation and subsequent dissolution of the precipitate thought to form as a result of the breakdown of the Fe(III)-citrate. In pH 7 end point enrichment

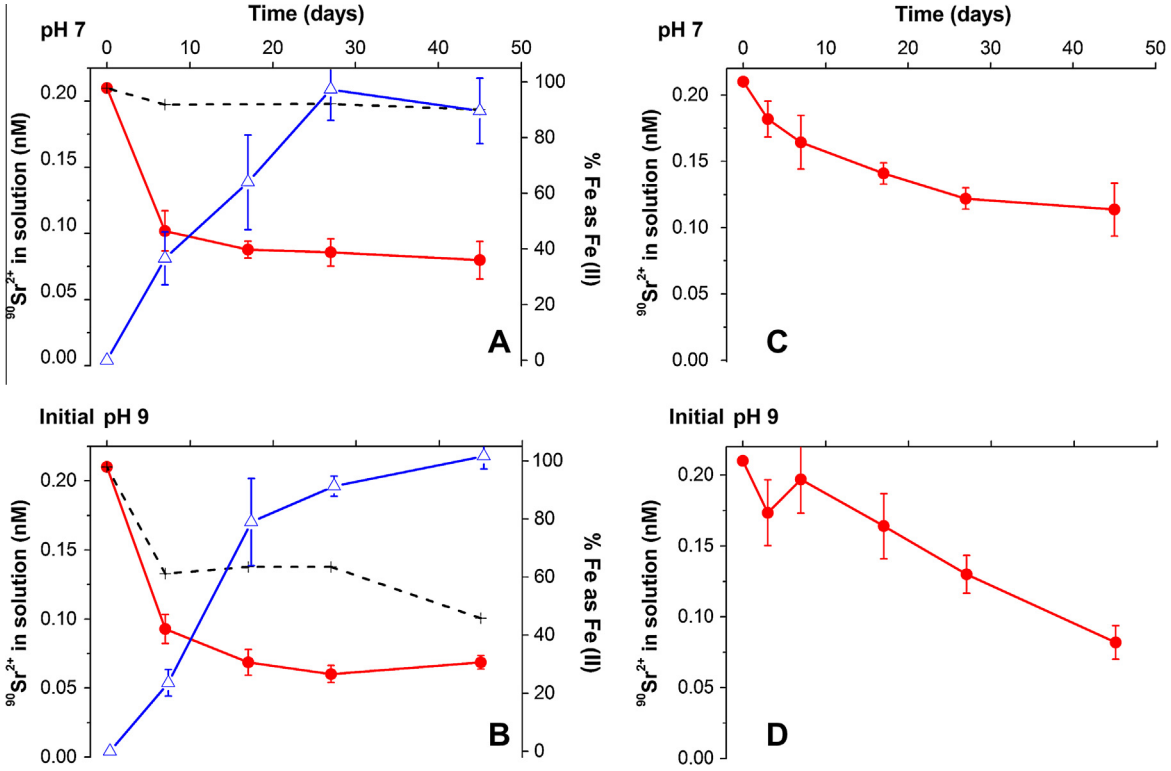

Fig. 3. $^{90}Sr^{2+}$ in solution (primary axis) and percentage of 0.5 N HCl extractable Fe present as Fe(II) (secondary axis) in 2.2×10^{-10} M experiments for: (A) $^{90}Sr^{2+}$ amended progressive enrichment systems at pH 7.0; (B) $^{90}Sr^{2+}$ amended progressive enrichment systems at an initial pH 9.0; (C) $^{90}Sr^{2+}$ amended end point enrichment systems at pH 7.0; and (D) $^{90}Sr^{2+}$ amended end point enrichment systems at initial pH 9. Key: ● = $^{90}Sr^{2+}$ in solution in inoculated enrichment systems, + = $^{90}Sr^{2+}$ in solution in corresponding sterile control systems, and △ = % Fe as Fe(II) progressive enrichment systems. Error bars represent 1σ experimental uncertainty from triplicate experiments (where not visible error bars are within symbol size).

Table 2
Table of modelled log saturation indices (log SI) for key minerals in 1.15×10^{-3} M Sr^{2+} and 2.2×10^{-10} M experimental systems modelled in PHREEQC-2 where log SI = log (Ion Activity Product/Solubility Product).

System	Siderite	Strontianite 1.15×10^{-3} M Sr^{2+}	Strontianite 2.2×10^{-10} M Sr^{2+}	Vivianite	Haematite	Goethite	$Fe(OH)_3$
Reduced pH 7	3.17	0.62	−6.15	10.2	–	–	–
Reduced pH 9	4.80	3.05	−4.47	14.7	–	–	–
Oxic pH 7	–	0.80	−5.91	–	25.8	11.0	6.15
Oxic pH 9	–	1.72	−3.96	–	26.2	12.1	6.37

systems, where the stable Sr^{2+} was reacted with the pre-formed biomineral, reactivity was also low (14.1 ± 2.3% removed from solution; Fig. 4C). Modelling of this system in PHREEQC-2 predicted that $SrCO_3$ was modestly oversaturated with a saturation index of +0.63 (Table 2), however, no direct XRD or morphological evidence for $SrCO_3$ precipitation was observed. Geochemical analyses coupled to sequential extractions performed on materials taken from the end point enrichment system indicated that of the total stable strontium in the system, 82.3 ± 2.0% of Sr^{2+} was in solution, 7.2 ± 1.8% of Sr^{2+} was in the exchangeable fraction, 4.1 ± 2.1% was in the carbonate associated fraction, and 6.4 ± 0.7% was in the reducible fraction: the system was dominated by soluble Sr^{2+}.

3.2.4.2. Stable strontium behaviour at pH 9. In the pH 9 oxic sterile control amended with 1.15×10^{-3} M of Sr^{2+}, the added strontium became associated (>80%) with the abiotically precipitated Fe(III) mineral phase by 20 days (Fig. 4B). In the pH 9 progressive enrichment systems the strontium was largely partitioned to the solid phase throughout bioreduction and after 45 days of incubation 90.5 ± 0.1% of the added Sr^{2+} was removed from solution (Fig. 4B). In the parallel end point enrichment systems where stable strontium was added to the pre-formed biomineral at pH 9, removal was rapid with 93.3 ± 2.2% removed from solution within 5 days (Fig. 4D). Overall, this suggests significant retention of Sr^{2+} in the sterile control in the presence of the amorphous Fe(III) precipitate that formed at high pH. In addition, for the microbially active experiment, there was strong retention of Sr^{2+} in the high pH system throughout the biogeochemical changes induced by Fe(III)-reduction. Solution modelling of the end point enrichment system predicted that it was significantly oversaturated with respect to $SrCO_3$ (SI = +3.05; Table 2). The relatively low stable Sr^{2+} concentrations used in the experiments made detection of $SrCO_3$ beyond the limits of XRD analysis although ESEM imaging and EDAX analysis (Fig. 5), showed aggregates of acicular strontium rich crystals typical of strontianite morphology. Sequential extractions performed on the end point enrichment system showed that of the total stable strontium in the system, 6.7 ± 3.4% was present in solution, 20.7 ± 6.6% of Sr^{2+} was exchangeable, 62.7 ± 6.5% was carbonate associated, and 8.3 ± 1.5% was associated with reducible phases. These results suggest that the majority (>70% of the Sr^{2+} in pH 9 end point system) required a strong chemical leaching agent for remobilisation. Furthermore, a significant fraction of the Sr^{2+} was likely associated with carbonates and in line with previous sediment microcosm experiments (Thorpe et al., 2012a). Interestingly, in the oxic pH 9 sterile control, minerals with strontianite crystal structure or morphology were not detected by XRD or ESEM respectively over the timescale of the experiment, even though systems were predicted to be oversaturated with regard to $SrCO_3$ (Table 2). The microbially active systems may favour strontianite formation either because of increased CO_3^{2-} in the system that results from microbial Fe(III) reduction and/or due to the presence of microbial cells and/or biogenic siderite crystals that may have provided nucleation sites to catalyse new biomineral formation (Schultze-Lam and Beveridge, 1994; Parmar et al., 2000; Roden et al., 2002; Douglas, 2004).

It is important to treat sequential extraction data as providing "operationally defined" insights into trace element behaviour. Indeed, vivianite is known to be extracted across carbonate and extractable fractions (Dodd et al., 2000). Nonetheless, in the model systems presented in this study the evidence provided by sequential extractions supports significant retention of $^{90}Sr^{2+}$ by Fe(II)-bearing biomineral phases at low concentrations (2.2×10^{-10} M) at both pH 7 and pH 9. At millimolar Sr^{2+}

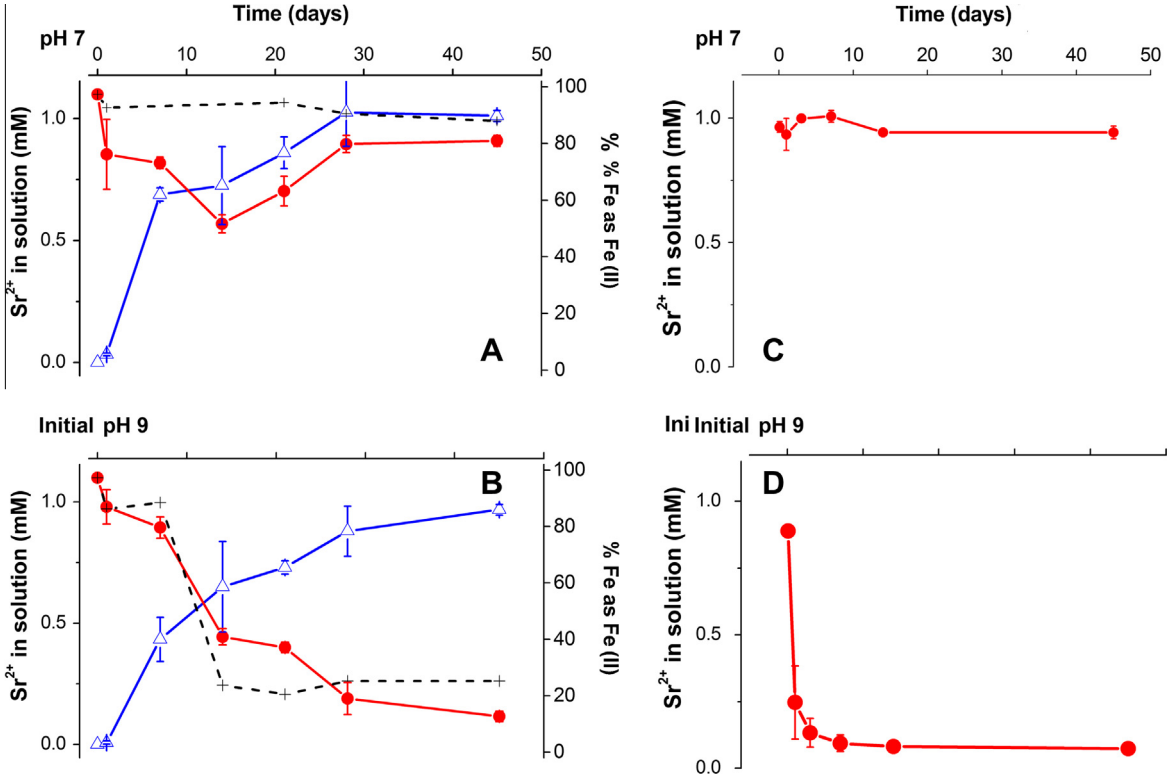

Fig. 4. The concentration of Sr^{2+} in solution (primary axis) and percentage of 0.5 N HCl extractable Fe present as Fe(II) (secondary axis) in 1.15 mM experiments for: (A) Sr^{2+} amended progressive enrichment systems at pH 7.0; (B) Sr^{2+} amended progressive enrichment systems at an initial pH 9.0; (C) Sr^{2+} amended end point enrichment systems at pH 7.0; and (D) Sr^{2+} amended end point enrichment systems at initial pH 9. Key: ● = Sr^{2+} in solution in inoculated enrichment systems, + = Sr^{2+} in solution in corresponding sterile control systems, and △ = % Fe as Fe(II) progressive enrichment systems. Error bars represent 1σ experimental uncertainty from triplicate experiments (where not visible error bars are within symbol size).

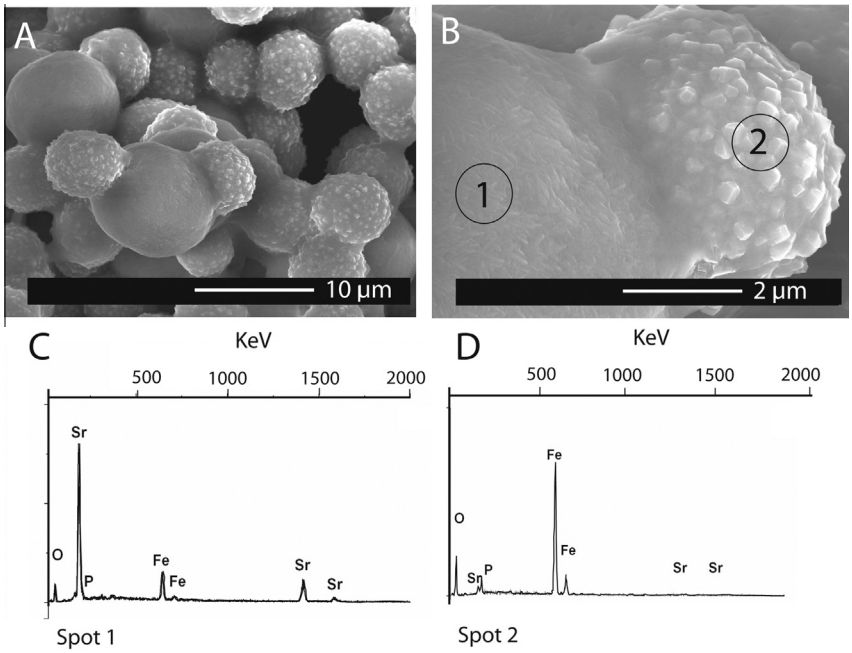

Fig. 5. ESEM images of a sample taken from an end point (45 days) Fe(II) biomineral system at pH 8.5 showing; (A) aggregates of acicular crystals typical of strontianite and aggregates of cubic crystals typical of siderite associated together; (B) a close up of associated siderite and strontianite aggregates on which EDAX spectra were taken; (C) EDAX spectrum of a Sr^{2+} rich aggregate (spot 1) identified as strontianite and (D) EDAX spectrum of a Fe rich aggregate identified as siderite (spot 2).

concentrations however, data show poor association with Fe(II)-bearing biominerals at pH 7. In pH 9 model systems with stable, millimolar strontium, morphological and chemical evidence for precipitation of strontianite in bioreduced experiments was presented highlighting that high pH systems typically show robust removal of Sr^{2+}.

3.2.4.3. Implications. Overall, this work demonstrates the potential for substantial removal of trace level Tc(VII) and $^{90}Sr^{2+}$ in systems containing biogenic siderite and vivianite at both pH 7 and 9 and the removal of millimolar concentrations of Sr^{2+} in pH 9 systems. Tc(VII) was removed by reductive precipitation to hydrous TcO_2 like phases, and $^{90}Sr^{2+}/Sr^{2+}$ by sorption/incorporation to the newly formed Fe(II) biomineral phases. Results demonstrated that contact with Fe(II) bearing biominerals under alkaline (pH 9) conditions caused removal of Tc(VII) at the same level as the pH 7 experiments and XAS confirmed reductive precipitation to hydrous $Tc(IV)O_2$ like phases. At trace $^{90}Sr^{2+}$ concentrations, (2.2×10^{-10} M) sequential extractions showed $^{90}Sr^{2+}$ had a strong association with the biomineral phases under both neutral and alkaline conditions. At millimolar concentrations however, Sr^{2+} showed poor sorption to the Fe(II) biominerals formed in the microbially active experiment at pH 7. By contrast, in pH 9 sterile controls, significant sorption to the Fe(III)-precipitate had occurred by 20 days whilst in microbially active experiments, strontium carbonate precipitation was postulated from morphological and sequential extraction data. These model systems provide insight into the effects of natural and stimulated Fe(III) reduction on the mobility of the problematic fission products ^{99}Tc and $^{90}Sr^{2+}$ at nuclear contaminated sites. Specifically, they highlight for the first time that at mildly alkaline pH, bioreduction treatment processes are favourable to technetium and strontium-90 co-treatment. This has clear implications for the implementation of bioremediation approaches to treat multiple contaminant plumes at nuclear licenced sites.

Acknowledgments

We thank Jon Fellowes, Alastair Bewsher and Paul Lythgoe for help in data acquisition. We thank Julian Cruickshank and the Sellafield Land Quality team for their collaboration and input. This work was supported by a studentship to Clare L Thorpe from the Engineering and Physical Science Research Council (EPSRC) as part of the Decommissioning, Immobilisation and Management of Nuclear Waste for Disposal (DIAMOND) consortium: Grant EP/F055412/1. We also acknowledge the support of the Natural Environment Research Council (Grant NE/H007768/1) and we thank Diamond Light Source for access to Beamline B18 (Proposal Numbers SP-7367 and SP-7593) that contributed to the results presented here.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2013.11.005.

References

Alliot, I., Alliot, C., Vitorge, P., Fattahi, M., 2009. Speciation of Tc(IV) in bicarbonate media. Environ. Sci. Technol. 43, 9174–9182.
Binsted, N., Strange, R.W., Hasnain, S.S., 1992. Constrained and restrained refinement in EXAFS data analysis with curved wave theory. Biochemistry 31, 12117–12125.
Burke, I.T., Boothman, C., Lloyd, J.R., Mortimer, R.J.M., Livens, F.R., Morris, K., 2005. Effects of progressive anoxia on the solubility of technetium in sediments. Environ. Sci. Technol. 39, 4109–4116.
Burke, I.T., Livens, F.R., Lloyd, J.R., Brown, A.P., Law, G.W.T., McBeth, J.M., Ellis, B.L., Lawson, R.S., Morris, K., 2010. The fate of technetium in reduced estuarine sediments: combining direct and indirect analysis. Appl. Geochem. 25, 233–241.
Dobbin, P.S., Carter, J.P., San Juan, C.G.S., von Hobe, M., Powell, A.K., Richardson, D.J., 1999. Dissimilatory Fe(III) reduction by *Clostridium beijenrickii* isolated from freshwater sediment using Fe(III) maltol enrichment. FEMS Microbiol. Lett. 176, 131–138.
Dodd, J., Large, D.J., Fortey, N.J., Milodowski, A.E., Kemp, S., 2000. A petrographic investigation of two sequential extraction techniques applied to anaerobic canal bed mud. Environ. Geochem. Health 22, 281–296.
Douglas, S., 2004. Microbial biosignatures in evaporite deposits: evidence from Death Valley, California. Planet. Space Sci. 52, 223–227.
Ferris, F.G., Roden, E.E., 2000. Microbial Mineral Transformations at the Fe(II)/Fe(III) Redox Boundary for Solid Phase Capture of Strontium and other Metal/Radionuclide Contaminants. DOE. Report DOE/ER/62317.

Ferris, F.G., Hallberg, R.O., Lyvén, B., Pedersen, K., 2000. Retention of strontium, cesium, lead and uranium by bacterial iron oxides from a subterranean environment. Appl. Geochem. 15, 1035–1042.
Francis, A.J., Dodge, C.J., 1993. Influence of complex structure on the biodegradation of iron-citrate complexes. Appl. Environ. Microbiol. 59, 109–113.
Gurman, S.J., Binsted, N., Ross, I., 1984. A rapid, exact curved-wave theory for EXAFS calculations. J. Phys. C: Solid State Phys. 17, 143–151.
Islam, F.S., Pederick, R.L., Gault, A.G., Adams, L.K., Polya, D.A., Charnock, J.M., Lloyd, J.R., 2005. Interactions between the Fe(III)-reducing bacterium *Geobacter sulfurreducens* and arsenate, and capture of the metalloid by biogenic Fe(II). Appl. Environ. Microbiol. 71, 8642–8648.
Istok, J.D., Senko, J.M., Krumholz, L.R., Watson, D., Bogle, M.A., Peacock, A., Chang, Y.J., White, D.C., 2004. In situ bioreduction of technetium and uranium in a nitrate-contaminated aquifer. Environ. Sci. Technol. 38, 468–475.
Keith-Roach, M.J., Morris, K., Dahlgaard, H., 2003. An investigation into technetium binding in sediments. Mar. Chem. 81, 149–162.
Konhauser, K.O., 1997. Bacterial iron biomineralisation in nature. FEMS Microbiol. Rev. 20, 315–326.
Langley, S., Gault, A.G., Ibrahim, A., Takahashi, Y., Renaud, R., Fortin, D., Clark, I.D., Ferris, F.G., 2009. Strontium desorption from bacteriogenic iron oxides (BIOS) subjected to microbial Fe(III) reduction. Chem. Geol. 262, 217–228.
Law, G.T.W., Geissler, A., Boothman, C., Burke, I.T., Livens, F.R., Lloyd, J.R., Morris, K., 2010. Role of nitrate in conditioning aquifer sediments for technetium bioreduction. Environ. Sci. Technol. 44, 150–155.
Lear, G., McBeth, J.M., Boothman, C., Gunning, D.J., Ellis, B.L., Lawson, R.S., Morris, K., Burke, I.T., Bryan, N.D., Brown, A.P., Livens, F.R., Lloyd, J.R., 2010. Probing the biogeochemical behaviour of technetium using a novel nuclear imaging approach. Environ. Sci. Technol. 44, 156–162.
Lehours, A., Rabiet, M., Morel-Desrosiers, N., Morel, J., Jouve, L., Arbeile, B., Mailhot, G., Fonty, G., 2010. Ferric iron reduction by fermentative strain BS2 isolated from an iron-rich anoxic environment (Lake Pavin, France). Geomicrobiol. J. 27, 714–722.
Lloyd, J.R., Sole, V.A., Van Praagh, C.V.G., Lovley, D.R., 2000. Direct and Fe(II)-mediated reduction of technetium by Fe(II) reducing bacteria. Appl. Environ. Microbiol. 66, 3743–3749.
Lovley, D.R., Phillips, E.J.P., Lonergan, D.J., 1991. Enzymatic versus non-enzymatic mechanisms for Fe(III) reduction in aquatic sediments. Environ. Sci. Technol. 25, 1062–1067.
Lovley, D.R., Phillips, E.J.P., 1986. Availability of ferric iron for microbial reduction in bottom sediments of the fresh-water tidal Potomac River. Appl. Environ. Microbiol. 52, 751–757.
Lovley, D.R., Phillips, E.J.P., 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. Appl. Environ. Microbiol. 54, 1472–1480.
Lukens, W.W., Bucher, J.J., Edelstein, N.M., Shuh, D.K., 2002. Products of pertechnetate radiolysis in highly alkaline solution: structure of $TcO_2{\cdot}xH_{(2)}O$. Environ. Sci. Technol. 36, 1124–1129.
McBeth, J.M., Lear, G., Morris, K., Burke, I.T., Livens, F.R., Lloyd, J.R., 2007. Technetium reduction and reoxidation in aquifer sediments. Geomicrobiol. J. 24, 189–197.
McBeth, J.M., Lloyd, J.R., Law, G.T.W., Livens, F.R., Burke, I.T., Morris, K., 2011. Redox interactions of technetium with iron-bearing minerals. Miner. Mag. 75, 2419–2430.
McKenzie, H.M., Coughlin, D., Laws, F., Stamper, A., 2011. Sellafield Ltd. Groundwater Annual Report 2011. Sellafield Ltd.
Morris, K., Livens, F.R., Charnock, J.M., Burke, I.T., McBeth, J.M., Begg, J.D.C., Boothman, C., Lloyd, J.M., 2008. An X-ray absorption study of the fate of technetium in reduced and reoxidised sediments and mineral phases. Appl. Geochem. 23, 603–617.
Parmar, N., Warren, L.A., Roden, E.E., Ferris, F.G., 2000. Solid phase capture of strontium by the iron reducing bacteria *Shewanella alga* strain BrY. Chem. Geol. 169, 281–288.
Peretyazhko, T., Zachara, J.M., Heald, S.M., Jeon, B.H., Kukkadapu, R.K., Liu, C., Moore, D., Resch, C.T., 2008. Heterogeneous reduction of Tc(VII) by Fe(II) at the solid–water interface. Geochim. Cosmochim. Acta 72, 1521–1539.
Plymale, A.E., Fredrickson, J.K., Zachara, J.M., Dohnalkova, A.C., Heald, S.M., Moore, D.A., Kennedy, D.W., Marshall, M.J., Wang, C.M., Resch, C.T., Nachimuthu, P., 2011. Competitive reduction of pertechnetate (TcO_4^-)-Tc-99) by dissimilatory metal reducing bacteria and biogenic Fe(II). Environ. Sci. Technol. 45, 951–957.
Poston, T.M., Duncan, J.P., Dirkes, R.L., 2011. Hanford Site Environmental Report for Calendar Year 2010.PNL-10574.Pacific Northwest Laboratory. Richland, Washington.
Ravel, B., Newville, M., 2005. Athena, Artemis, Hephaestus: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12, 537–541.
Rizoulis, A., Steele, H.M., Morris, K., Lloyd, J.R., 2012. The potential impact of microbial metabolism during the geodisposal of intermediate level waste. Miner. Mag. 76, 3261–3270.
Roden, E.E., Leonardo, M.R., Ferris, F.G., 2002. Immobilization of strontium during iron biomineralization coupled to dissimilatory hydrous ferric oxide reduction. Geochim. Cosmochim. Acta 66, 2823–2839.
Schultze-Lam, S., Beveridge, T.J., 1994. Nucleation of celestite and strontianite on a cyanobacterial S-layer. Appl. Environ. Microbiol. 60, 447–453.
Stewart, D.I., Burke, I.T., Hughes-Berry, D.V., Whittleston, R.A., 2010. Microbially mediated chromate reduction in soil contaminated by highly alkaline leachate from chromium containing waste. Ecol. Eng. 36, 211–221.
Tenderholt, A., Hedman, B., Hodgson, K.O., 2007. PySpline: A modern, cross-platform program for the processing of raw averaged XAS edge and EXAFS data. In: X-ray Absorption Fine Structure-XAFS13, pp. .
Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedures for the speciation of particulate trace-metals. Anal. Chem. 51, 844–851.
Thorpe, C.L., Lloyd, J.R., Law, G.T.W., Burke, I.T., Shaw, S., Bryan, N.D., Morris, K., 2012a. Strontium sorption and precipitation behaviour during bioreduction in nitrate impacted sediments. Chem. Geol. 306, 114–122.
Thorpe, C.L., Law, G.T.W., Boothman, C., Lloyd, J.R., Burke, I.T., Morris, K., 2012b. Synergistic effect of high nitrate concentrations on sediment bioreduction. Geomicrobiol. J. 29, 484–493.
Tomic, S., Searle, B.G., Wander, A., Harrison, N.M., Dent, A.J., Mosselmans, J.F., Inglesfield, J.E., 2005. New Tools for the Analysis of EXAFS: the DL_EXCURV Package. CCLRC Technical Report DL-TR-2005-00, ISSN 1362–0207, Daresbury SRS 2005.
Vandehey, N.T., O'Neil, J.P., Slowey, A.J., Boutchko, R., Druhan, J.L., Moses, W.W., Nico, P.S., 2012. Monitoring Tc dynamics in a bioreduced sediment: an investigation with gamma camera imaging of Tc-99m-pertechnetate and Tc-99m-DTPA. Environ. Sci. Technol. 46, 12583–12590.
Wall, N.A., Karunathilake, N., 2012. Interactions of Tc(IV) with citrate in NaCl media. *Radiochim. Acta*. 101, 111–116.
Wallace, S.H., Shaw, S., Morris, K., Small, J.S., Fuller, A.J., Burke, I.T., 2012. Effect of groundwater pH and ionic strength on strontium sorption in aquifer sediments: implications for $90Sr^{2+}$ mobility at contaminated nuclear sites. Appl. Geochem. 27, 1482–1491.
Wallace, S.H., Shaw, S., Morris, K., Small, J.S., Burke, I.T., 2013. Alteration of sediments by hyperalkaline k-rich cement leachate: implications for strontium adsorption and incorporation. Environ. Sci. Technol. 47, 3694–3700.
Wharton, M.J., Atkins, B., Charnock, J.M., Livens, F.R., Pattrick, R.A.D., Collison, D., 2000. An X-ray absorption spectroscopy study of the co-precipitation of Tc and Re with mackinawite (FeS). Appl. Geochem. 15, 347–354.
Whittleston, R.A., Stewart, D.I., Mortimer, R.J.G., Ashley, D.J., Burke, I.T., 2011. Effect of microbially induced anoxia on Cr(VI) mobility at a site contaminated with hyperalkaline residue from chromite ore processing. Geomicrobiol. J. 28, 68–82.
Williamson, A.J., Morris, K., Shaw, S., Byrne, J.M., Boothman, C., Lloyd, J.R., 2013. Microbial reduction of Fe(III) under alkaline conditions relevant to geological disposal. Appl. Environ. Microbiol. 79, 3320–3326.